

NOV 7 1972

LIBRARY AND  
DOCUMENTS SECTION

NOZZLE BEAMS, A SOURCE OF MOLECULES  
WITH INTRIGUING PROPERTIES

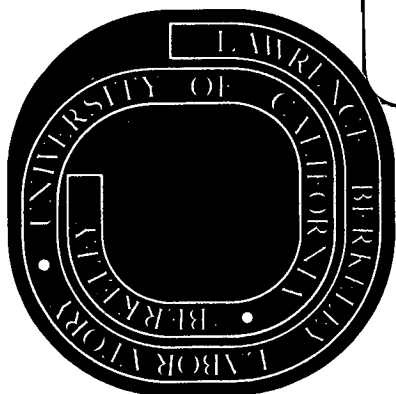
Steven L. Bernasek and G. A. Somorjai

November 1972

Prepared for the U.S. Atomic Energy  
Commission under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545



LBL-1140

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

NOZZLE BEAMS, A SOURCE OF MOLECULES  
WITH INTRIGUING PROPERTIES

Steven L. Bernasek and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory  
and Department of Chemistry, University of California  
Berkeley, California 94720

ABSTRACT

The production of a beam of molecules by expansion through a high velocity nozzle is discussed and compared with beams of molecules emanating from an effusion source. Many of the interesting properties of these nozzle produced beams (large average velocity, low beam temperature, narrow energy distribution, angular distribution peaked along the nozzle centerline, production of atom clusters in the beam) are reviewed. These properties have made the nozzle source a valuable experimental tool of the chemist.

The aerodynamic properties of rapidly expanding high pressure gases have been of great importance in the aeronautical sciences for some time. Since the pioneering work of Kantrowitz and Grey,<sup>1</sup> and of Kistiakowsky and Schlichter,<sup>2</sup> rapidly expanding jets of gas have found interesting chemical applications.

When a gas stream emerges from a nozzle source (to be described below) at supersonic speeds, the gas atoms may have kinetic energies of a few electron volts ( $1 \text{ eV} = 23 \text{ kcal}$ ). The gas atoms emerging from a  $300^\circ\text{K}$  effusion source have average kinetic energies of  $\sim 0.02 \text{ eV}$  in contrast. The intensities of nozzle produced beams can be orders of magnitude greater than the intensity of beams produced by an effusion source. (Typical values are  $\sim 1 \times 10^{17} \text{ cm}^{-2} \text{ sec}^{-1}$  for a nozzle source as compared to  $\sim 5 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$  for an effusion source.<sup>3</sup>) In addition, the velocity distribution of particles leaving the nozzle source correspond to beam temperatures much lower than the temperature of the source enclosure, as will be seen below. This cooling can even result in the formation of atom clusters<sup>4</sup> which cannot be formed and studied conveniently any other way.

The construction of the nozzle source is shown in Fig. 1. The nozzle beam is created by expanding the gas through a converging nozzle from a high pressure (1-1000 torr) enclosure, into an evacuated chamber ( $< 10^{-3}$  torr). Downstream of the nozzle opening, a skimmer is placed whose purpose is to collimate the emerging beam without allowing back-scattering into the source area.

By contrast, the effusion source, that is shown in Fig. 2, is used customarily to create a beam of gas particles by the random effusion of

the gas through an opening between an effusion oven at relatively low pressure ( $< 10$  torr) and a chamber at vacuum. The effusion beam is collimated by one or more orifices downstream of the source opening.

It is customary to define  $Kn_o$ , the Knudsen number, to estimate the number of collisions of gas atoms emerging from the source opening. It is given by

$$Kn_o = \frac{\lambda}{w}$$

where  $\lambda = \frac{\bar{u}}{z}$ , the mean free path (average velocity divided by collision rate), and  $w$  is the source opening diameter.

For a nozzle with the dimensions of Fig. 1, operating at a pressure of 100 torr with argon at 300°K, the Knudsen number is calculated to be  $1.14 \times 10^{-3}$ .

$$Kn_o = \frac{\lambda}{w} = \frac{1}{\sqrt{2} \pi N d^2 w}$$

$$\text{where } N = \text{atoms/cm}^3 = (6.02 \times 10^{23}) n = \frac{6.02 \times 10^{23} PV}{RT}$$

(from the ideal gas law), and  $d$  is the atomic diameter = 2.86Å for argon.<sup>5</sup>

The average velocity  $\bar{u}$  is given by

$$\bar{u} = \left( \frac{8RT}{\pi M} \right)^{1/2} = 3.98 \times 10^4 \text{ cm/sec}$$

where  $M$  is the molecular weight of the gas, for argon at 300°K. Therefore, the number of collisions in the nozzle of Fig. 1 is

$$z = \bar{u}/\lambda = \bar{u}/Kn_o w$$

$$z = \frac{3.98 \times 10^4 \text{ cm} \cdot \text{sec}^{-1}}{(1.14 \times 10^{-3})(7.5 \times 10^{-2} \text{ cm})}$$

$$z = 4.65 \times 10^8 \text{ sec}^{-1}$$

This high collision rate in the emerging nozzle beam should be contrasted with the collision rate in the opening of the effusion source of Fig. 2. For effusive flow, the mean free path of the effusing atoms must be greater than or equal to the dimensions of the opening. This means that the Knudsen number for an effusion source could be unity at the least. For the effusion source of Fig. 2, operating at  $1 \times 10^{-1}$  torr with argon at  $300^\circ\text{K}$ , the Knudsen number is 1.14. The collision rate for this effusion source is then  $4.65 \times 10^5 \text{ sec}^{-1}$ .

The ideal operating condition for the effusive source is low pressure (i.e., the mean free path of the particles is  $\geq$  the orifice size,  $\sim 10^{-1}$  torr in this case). The nozzle source is operated at higher pressures ( $> 10^{-1}$  torr).

The advantage in beam intensity gained by using higher source pressures is obvious. It is interesting to compare the equations governing the intensity of particles emerging from the effusion source and the nozzle source.<sup>3</sup>

$$I_{\text{eff}} = \frac{\bar{u}w}{16\sqrt{2} \pi d^2 l^2}$$

where  $l$  is the distance from the opening.

$$I_{\text{nozzle}} = \pi r_1^2 n_1 \bar{u}' \left( \frac{\gamma}{2} M^2 + \frac{3}{2} \right) \frac{1}{\pi l^2}$$

where  $r_1$  is the skimmer diameter,  $n_1$  is the particle density in the source,  $\bar{u}'$  is the velocity of the particles along the nozzle centerline,  $\gamma$  is the ratio of specific heats ( $C_p/C_v$ ) for the gas, and  $M$  is the Mach number. The Mach number is related to the Knudsen number for a particular gas by

the relationship<sup>6</sup>

$$M = A \text{Kn}_o^{-B}$$

where A and B are positive constants. For a particular nozzle geometry and source gas,  $r_1$  and  $\gamma$  are constants. The Mach number, number density and  $\bar{u}$  all depend on the source pressure. The intensity behavior as a function of pressure is shown in Fig. 3 for the nozzle source and the effusion source. As the figure shows, the intensity from the effusion source is independent of pressure in the source beyond the pressure  $P'$ . This is the pressure corresponding to a Knudsen number of 1.0 for the geometry of Fig. 2. In the nozzle source case, however, the intensity increases with pressure because of the increase in Mach number, number density and axial average velocity.

It is also interesting to compare the angular distribution of the particles emerging from the two types of molecular beam sources, as shown in Fig. 4. The curves show intensity contours as a function of angle from the beam centerline. The effusion source shows the cosine distribution of particles randomly emerging from the opening, while the nozzle source shows a distribution peaked along the centerline because of jet motion along the nozzle axis.

The expansion of the gas through the nozzle source can be viewed as an adiabatic and reversible expansion. It is instructive to review the thermodynamics of this type of expansion in order to compute and compare the kinetic energies of the beams produced by the nozzle and effusive sources.

From the First Law of Thermodynamics, we have

$$dE = dq - dw \quad (1)$$

where  $dE$  is the differential change in internal energy of the system,  $dq$  is the differential heat change, and  $dw$  is the differential work. For an adiabatic, reversible expansion,  $dq = 0$  and Eq. (1) can be written

$$-dE = dw = PdV \quad (2)$$

where  $P$  is pressure and  $dV$  is differential volume change, since only expansion work takes place. Since  $E = E(T, V)$ ,  $dE$  can be written

$$dE = \left( \frac{\partial E}{\partial V} \right)_T dV + \left( \frac{\partial E}{\partial T} \right)_V dT \quad (3)$$

For an ideal gas  $\left( \frac{\partial E}{\partial V} \right)_T = 0$ , so  $dE$  becomes

$$dE = \left( \frac{\partial E}{\partial T} \right)_V dT = C_V dT = -PdV \quad (4)$$

where  $C_V$  is the heat capacity at constant volume. Using the ideal gas law for one mole of gas ( $PV=RT$ ),

$$C_V dT = - \frac{RTdV}{V}$$

or

$$\frac{C_V}{T} dT = - \frac{RdV}{V} \quad (5)$$

Integrate this expression from  $T_o \rightarrow T$  and  $V_o \rightarrow V$  to obtain

$$C_V \ln \frac{T}{T_o} = -R \ln \frac{V}{V_o} \quad (6)$$

or

$$\left( \frac{T}{T_o} \right)^{C_V} = \left( \frac{V}{V_o} \right)^{-R}$$



This can also be written as

$$\frac{T}{T_0} = \left( \frac{V_0}{V} \right)^{R/C_V} \quad (7)$$

$T_0$  and  $V_0$  are the temperature and volume of the gas before expansion, i.e., in the nozzle source.  $V$  is the volume to which the gas is expanded and  $T$  is the temperature of the expanded gas, i.e., the beam temperature.\* By expanding from a small volume to a large volume (high pressure to low pressure), the temperature of the beam can be much lower than the temperature of the source.

For the effusion source, the temperature of the beam is the same as the temperature of the source since only random effusion takes place. The effect of the cooling on expansion is shown in Fig. 5 which compares the velocity distributions for beams at 300°K (effusion source) and 50°K (nozzle source).

Because of the cooling upon expansion and the axial velocity component of the beam produced by a nozzle source, the energy of the nozzle beam is greater than the energy of the effusive beam. This can be shown as follows:

$$\bar{E}_{\text{eff}} = 3/2 RT_0 = \bar{E}_{\text{thermal}} \quad (8)$$

For a nozzle source (after expansion)

$$\bar{E}_{\text{nozzle}} = \bar{E}_{\text{thermal}} + \frac{m\bar{u}'^2}{2} \quad (9)$$

where  $\frac{m\bar{u}'^2}{2}$  is the average kinetic energy added due to the net motion of the particles of mass  $m$  and average velocity  $\bar{u}'$  along the axis of the nozzle. This term is not present for the effusion source because the flow from the effusion opening is random. By the First Law,

\*Beam temperature refers to a temperature characteristic of the velocity distribution of the beam molecules.

$$\bar{E}_{\text{thermal}} + \frac{\bar{m}\bar{u}^2}{2} = q - (w + w') \quad (10)$$

where  $w$  is PV work and  $w'$  is all other work (electrical, chemical).

However,  $q = 0$  since the expansion is adiabatic and  $w' = 0$  because only expansion work takes place. The initial energy state of the nozzle system (before expansion) is the same as for the effusive source. The final state (after expansion) is given by Eq. (9).

$$\begin{aligned} \Delta \bar{E} &= \bar{E}_{\text{final}} - \bar{E}_{\text{initial}} \\ &= \bar{E}_{\text{thermal,final}} - \bar{E}_{\text{thermal,initial}} + \frac{\bar{m}\bar{u}^2}{2} \end{aligned}$$

Using Eq. (10) this becomes

$$\Delta \bar{E}_{\text{thermal}} + \frac{\bar{m}\bar{u}^2}{2} + \Delta(PV) = 0 \quad (11)$$

where  $\Delta \bar{E}_{\text{thermal}} = \bar{E}_{\text{thermal,final}} - \bar{E}_{\text{thermal,initial}}$  and  $w$  has been replaced by  $\Delta(PV)$ .  $\Delta \bar{H} = \Delta \bar{E}_{\text{thermal}} + \Delta(PV)$ , so

$$\Delta \bar{H} + \frac{\bar{m}\bar{u}^2}{2} = 0 \quad (12)$$

$\Delta \bar{H} = \bar{H} - \bar{H}_0$ , where  $\bar{H}$  is the enthalpy of the expanded gas and  $\bar{H}_0$  is the enthalpy of the gas in the source, and  $\Delta \bar{H} = C_p \Delta T$ . Therefore, Eq. (12) becomes

$$C_p \Delta T + \frac{\bar{m}\bar{u}^2}{2} = 0 \quad (13)$$

Since  $\Delta T = T - T_0$ , Eq. (13) can be written

$$C_p (T_0 - T) = \frac{\bar{m}\bar{u}^2}{2} \quad (14)$$

$C_p$  is defined as  $\left(\frac{\partial H}{\partial T}\right)_p$  which can be approximated by  $C_p = \frac{\Delta \bar{H}}{\Delta T}$ , in the limit of  $\Delta T \rightarrow 0$ , which for an expansion to large volumes (low  $T$ ) is approximately  $\bar{H}_o/T_o$ .<sup>7</sup> Equation (14) becomes

$$\frac{\bar{m}\bar{u}^2}{2} = \frac{\bar{H}_o}{T_o} (T_o - T)$$

Rearranging

$$\frac{\bar{m}\bar{u}^2}{2} = \frac{\bar{H}_o}{\frac{T_o - T + T}{T_o - T}} = \frac{\bar{H}_o}{1 + \frac{T}{T_o - T}} \quad (15)$$

Finally, combining Eqs. (15) and (14),

$$\frac{\bar{H}_o}{1 + \frac{T}{T_o - T}} = C_p (T_o - T) \quad (16)$$

The energy ratio then becomes, using Eqs. (8), (9), and (16)

$$\begin{aligned} \frac{\bar{E}_{\text{nozzle}}}{\bar{E}_{\text{oven}}} &= \frac{C_p (T_o - T)}{\frac{3}{2} RT_o} = \frac{\bar{H}_o \left(1 + \frac{T}{T_o - T}\right)^{-1}}{\frac{3}{2} RT_o} \\ &= \frac{C_p T_o \left(1 + \frac{T}{T_o - T}\right)^{-1}}{\frac{3}{2} RT_o} \end{aligned}$$

$$\frac{\bar{E}_{\text{nozzle}}}{\bar{E}_{\text{oven}}} = \frac{2}{3} \frac{C_p}{R} \left[1 + \frac{T}{T_o - T}\right]^{-1} \quad (17)$$

As was shown in the discussion of the adiabatic reversible expansion, for the nozzle source  $T$  is much less than  $T_0$  because of the large volume increase upon expansion. Therefore the term in brackets approaches one, and Eq. (17) becomes

$$\frac{\bar{E}_{\text{nozzle}}}{\bar{E}_{\text{eff}}} \approx \frac{2}{3} \frac{C_p}{R}$$

$\frac{C_p}{R}$  can be written  $\frac{C_p/C_v}{R/C_v} = \frac{\gamma}{\gamma-1}$  in terms of the specific heat ratio  $\gamma$ . Thus the energy ratio can be expressed as

$$\frac{\bar{E}_{\text{nozzle}}}{\bar{E}_{\text{eff}}} \approx \frac{2}{3} \frac{\gamma}{\gamma-1} \quad (18)$$

For a source temperature of 2000°K,

$$\bar{E}_{\text{eff}} = 3/2(1.99 \text{ cal/mole deg})(2 \times 10^3 \text{ deg})$$

$$= 6.0 \times 10^3 \text{ cal/mole,}$$

$$\text{while } \bar{E}_{\text{nozzle}} (\text{monatomic gas, } \gamma = \frac{5}{3}) = \frac{2}{3} \left( \frac{7/5}{2/5} \right) (6 \times 10^3) = 1.4 \times 10^4 \text{ cal/mole}$$

A temperature of 2000°K is an upper limit for successful operation of a beam source because of materials limitations. For an effusion source to produce particles with an energy of 14 kcal/mole, it would have to be operated at a temperature of 4800°K, much higher than most present-day construction materials could withstand.

The adiabatic cooling of the gas upon expansion has another interesting consequence. Due to the narrow velocity distribution of the beam particles, the relative velocities of particles in the beam are very

similar. (See Fig. 6.) Therefore, on collisions between particles in the beam there is little transfer of kinetic energy. In fact, since  $\Delta E_{\text{collision}} \ll \Delta E_{\text{condensation}}$  clustering of atoms held together by weak Van der Waals forces can take place. Due to the high collision rates in the emerging beam, three body collisions can readily occur to carry away the heat of condensation. Of course, cluster formation is more prevalent if stronger forces of attraction (electrostatic) are present. The presence of large argon atom clusters was reported by Green and Milne,<sup>4</sup> and the generation of high intensity beams of dimers of alkali atoms ( $\text{Na}_2$ ) in nozzle beams was reported by Gordon, Lee and Herschbach.<sup>8</sup>

As was shown above, a nozzle source operating at 2000°K could produce particles with energies of 14 kcal/mole. Higher energy atoms can be produced with a nozzle beam by using a technique called "seeding." This involves using a mixture of a large mole fraction light gas with a small mole fraction heavy gas. For example, the "seeded" beam could be a mixture of 99 mole percent hydrogen with 1 mole percent carbon monoxide. At a given temperature, all of the particles will have a velocity distribution appropriate to a beam of molecules with the average mass. The heavy particles are speeded up and the light particles slowed down by the large number of collisions taking place in the emerging beam. The beam appears to have properties as if it were made up of pseudo-particles, all of whose masses are the arithmetic average of the actual molecular weights of the beam particles.

In the example above, this average mass would be

$$\frac{[99(2) + (1)(28)]}{100} = 2.26 \text{ grams/mole}$$

For a 2000°K nozzle source using this mixture of diatomic gases the particles will have 14 kcal/mole average energy. The average velocity of the particles can be found by equating the nozzle average energy with the kinetic energy of the particle.

$$\bar{E}_{\text{nozzle}} = \frac{7}{3} \bar{E}_{\text{thermal}} = 14 \text{ kcal/mole} = \frac{m\bar{u}'^2}{2} \quad (19)$$

where the factor 7/3 is from the ratio  $(\frac{\gamma}{\gamma-1})(\frac{2}{3})$  of Eq. (18). The average velocity is given by

$$\begin{aligned} \bar{u}' &= \left[ \frac{28 \text{ kcal/mole}}{m} \right]^{1/2} \\ &= \left[ \frac{24.9 \times 10^{10} \text{ ergs/mole}}{2.26 \text{ g/mole}} \right]^{1/2} = 4.68 \times 10^5 \text{ cm/sec} \end{aligned}$$

The pseudo particles of mass 2.26 will be traveling with an average velocity of  $4.68 \times 10^5$  cm/sec. Since all of the molecules are traveling with this average velocity, the CO molecules are traveling at a velocity corresponding to a much higher kinetic energy than otherwise possible. This energy can be calculated by using Eq. (19) again, this time substituting the CO molecular weight.

$$\frac{7}{3} \left( \frac{3}{2} RT_0 \right) = \frac{m\bar{u}'^2}{2} \quad (20)$$

Solving Eq. (20) for  $T_0$  gives

$$T_0 = \frac{m\bar{u}'^2}{7R}$$

So

$$T_0 = \frac{(2.8 \times 10^{-1} \text{ g/mole})(4.68 \times 10^5 \text{ cm/sec})^2}{7(8.314 \times 10^7 \text{ ergs/mole}^\circ\text{K})}$$

$$T_0 = 1.06 \times 10^4 \text{ }^\circ\text{K}$$

In other words, to produce a pure beam of CO molecules with energies of those in the "seeded" beam, the source temperature would have to be greater than 10,000°K. This source temperature (i.e. this velocity for CO molecules) corresponds to an energy of 70 kcal/mole which is in the range of chemical binding energies.

Of course this "seeding" technique creates problems of selectivity and detection because of the large amount of light gas present in the beam. If a system can be chosen where the light gas is ignored by the detector and can be pumped away efficiently, the "seeding" technique has obvious advantages for the creation of high velocity molecular beams.

**ACKNOWLEDGMENTS**

This work was supported by the U. S. Atomic Energy Commission. One of us (S.L.B.) gratefully acknowledges support of a Graduate Fellowship from the National Science Foundation.



REFERENCES

1. A. Kantrowitz and J. Grey, Rev. Sci. Instr. 22, 328 (1951).
2. G. B. Kistiakowsky and W. P. Schlichter, Rev. Sci. Instr. 22, 333 (1951).
3. J. B. Anderson, R. P. Andres and J. B. Fenn, High Intensity and High Energy Molecular Beams in Advances in Atomic and Molecular Physics 1, 345 (1965).
4. T. A. Milne and F. T. Greene, J. Chem. Phys. 47, 4095 (1967).
5. W. J. Moore, Physical Chemistry (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962) 3rd Ed., p. 229.
6. J. B. Anderson, R. P. Andres and J. B. Fenn, Supersonic Nozzle Beams in Advances in Chemical Physics 3, 275 (1966).
7. G. M. Barrow, Physical Chemistry (McGraw-Hill Book Company, New York, 1966), 2nd Ed., p. 136.
8. R. J. Gordon, Y. T. Lee and D. R. Herschbach, J. Chem. Phys. 54, 2393 (1971).

FIGURE CAPTIONS

- Fig. 1. Typical nozzle source geometry.
- Fig. 2. Typical effusion source.
- Fig. 3. Comparison of Intensity vs. Pressure Behavior for nozzle and effusion sources (after reference 8).
- Fig. 4. Contours of constant intensity for nozzle and effusion sources.
- Fig. 5. Maxwellian velocity distribution for  $T = 50^\circ\text{K}$  and  $300^\circ\text{K}$ .
- Fig. 6. Narrow distribution of nozzle produced beam at velocity corresponding to 14 kcal beam energy.

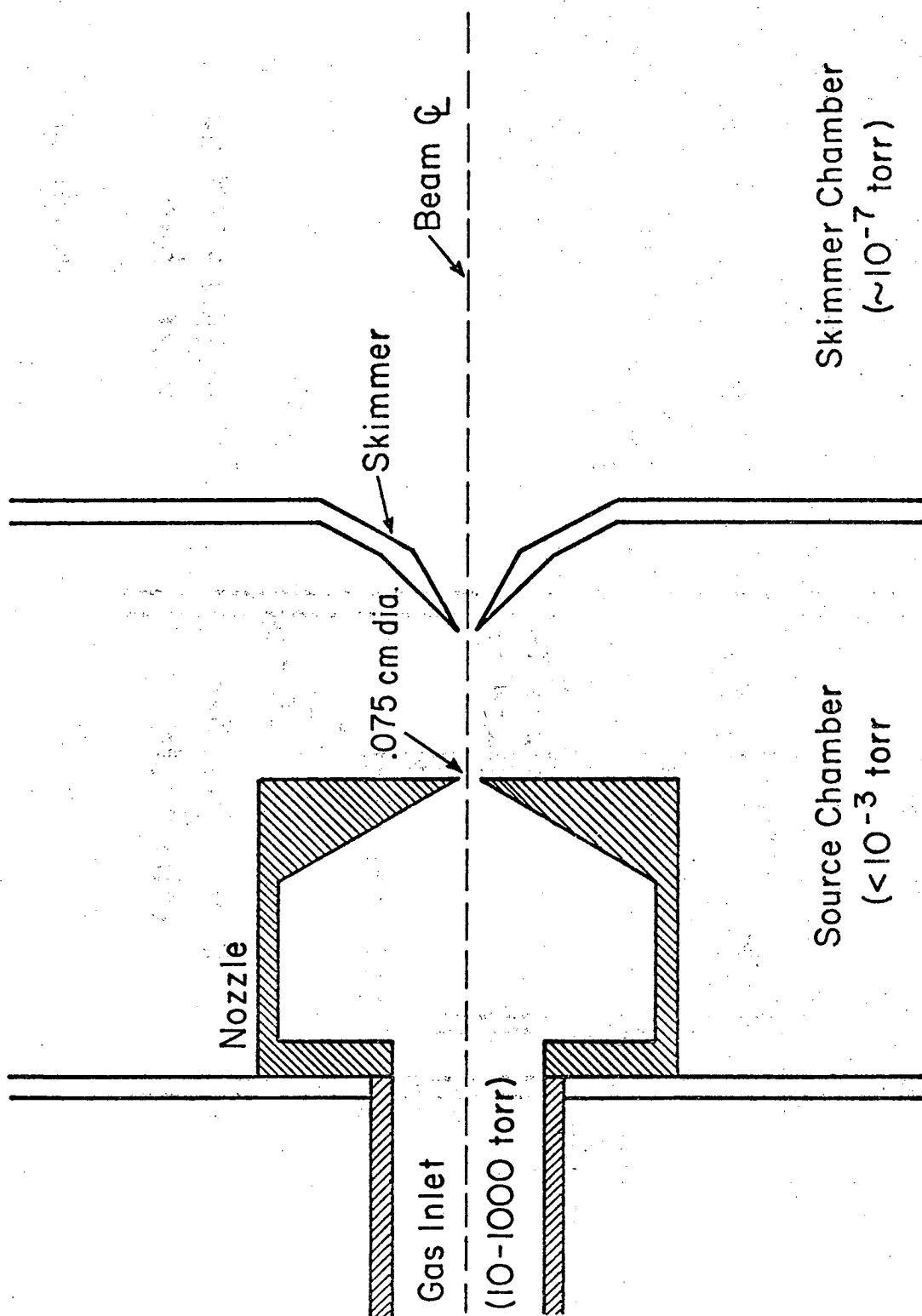
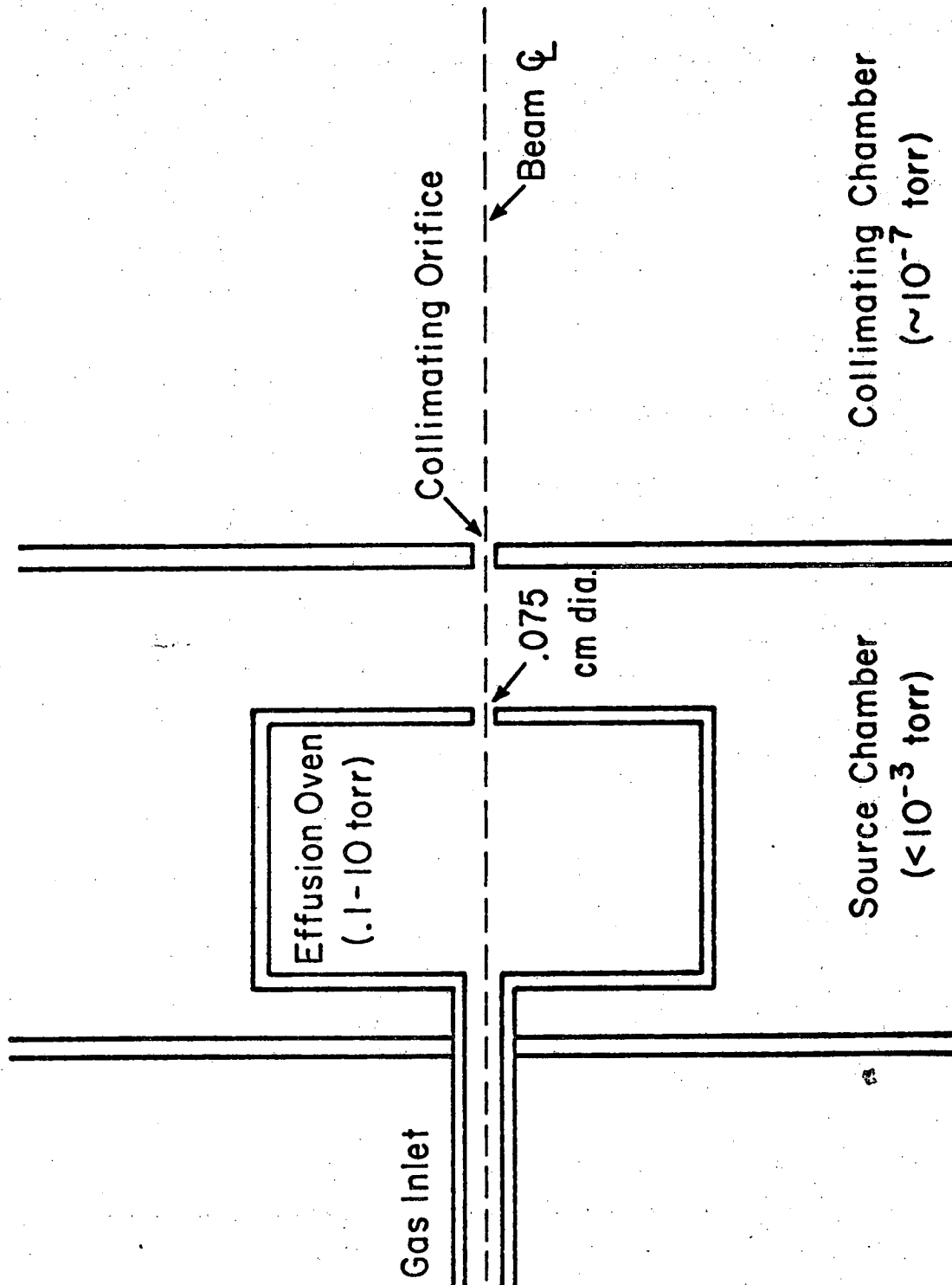


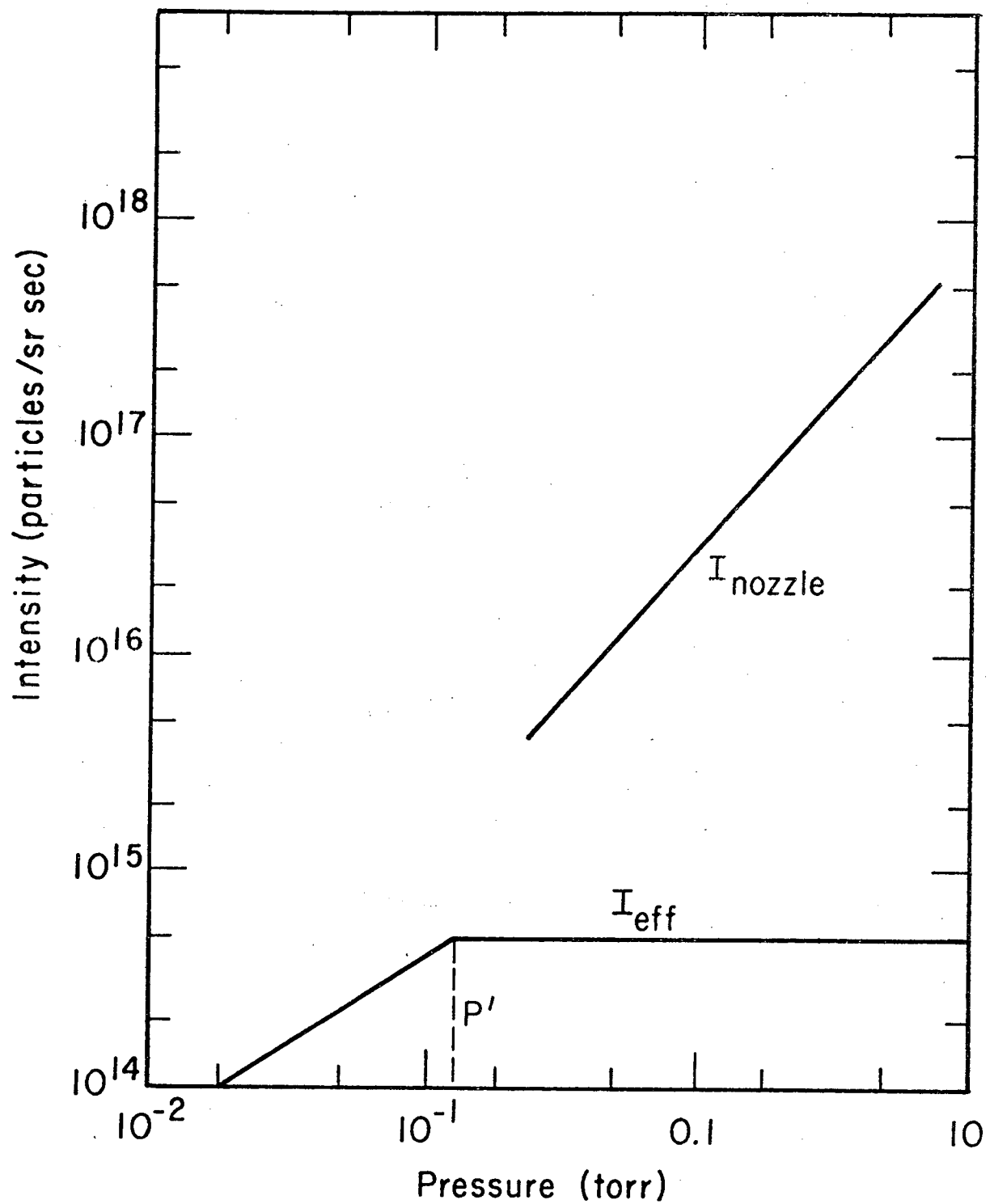
Fig. 1

XBL 7211-7165



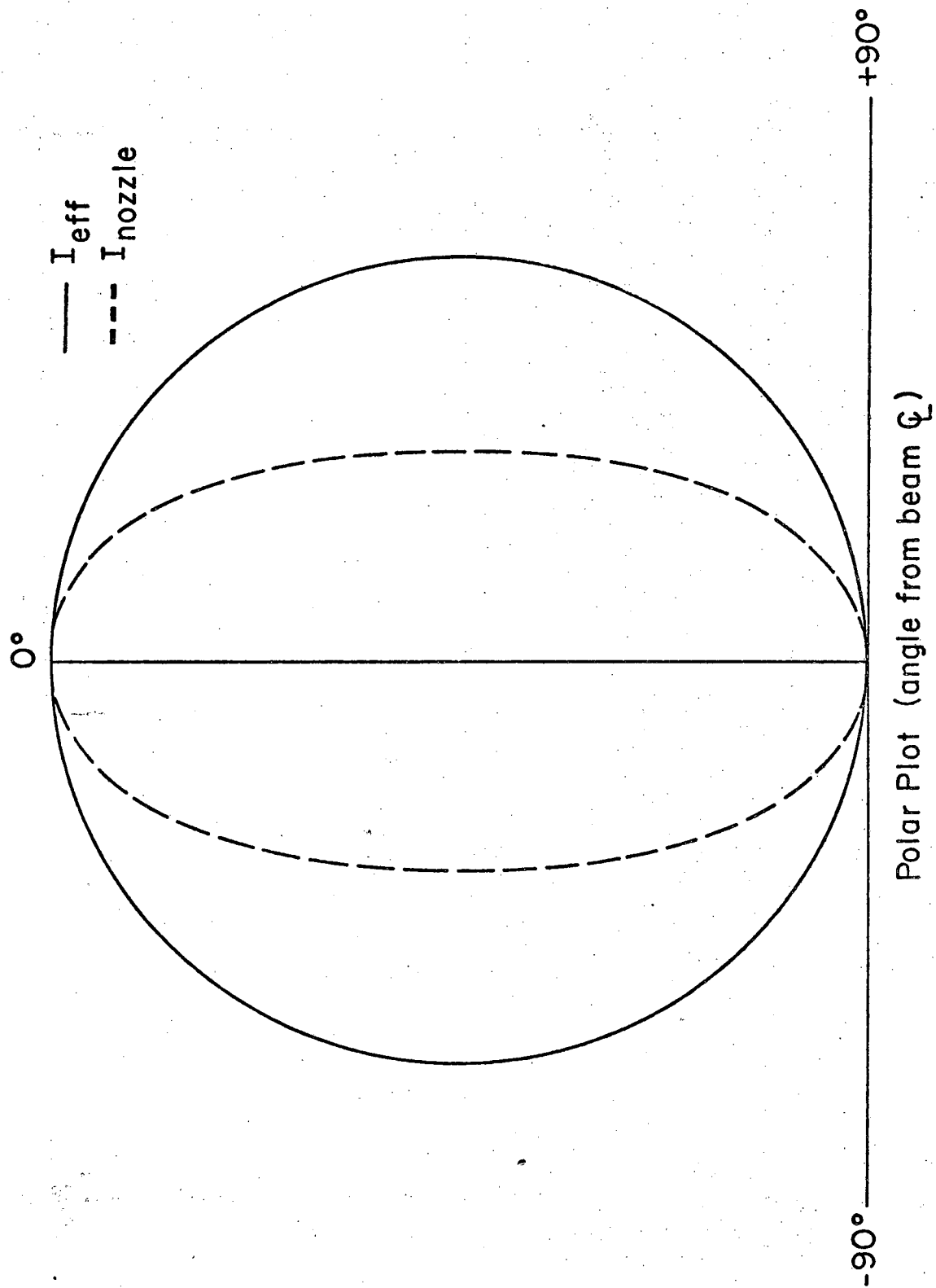
XBL 7211-7166

Fig. 2



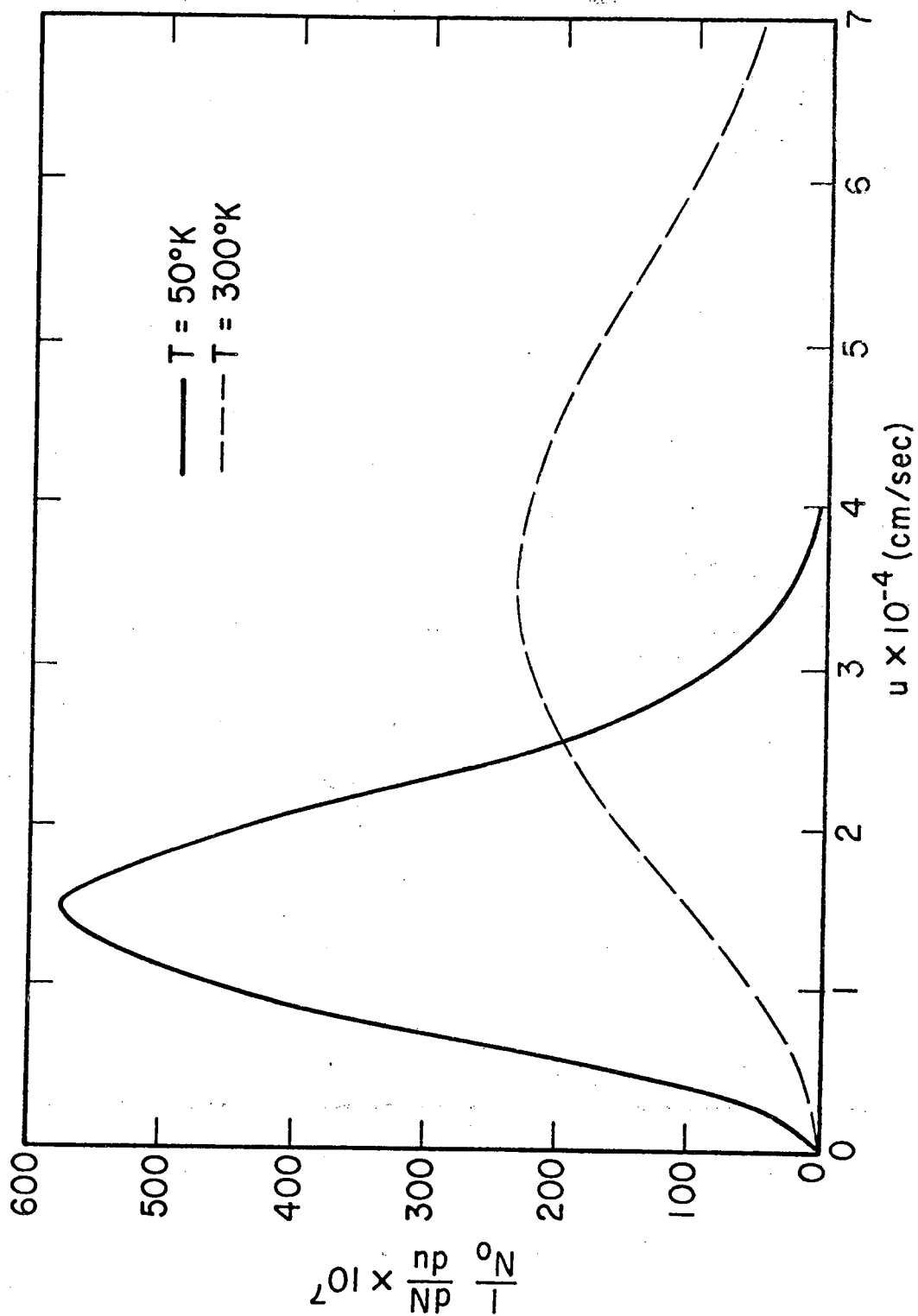
XBL 7211-7167

Fig. 3



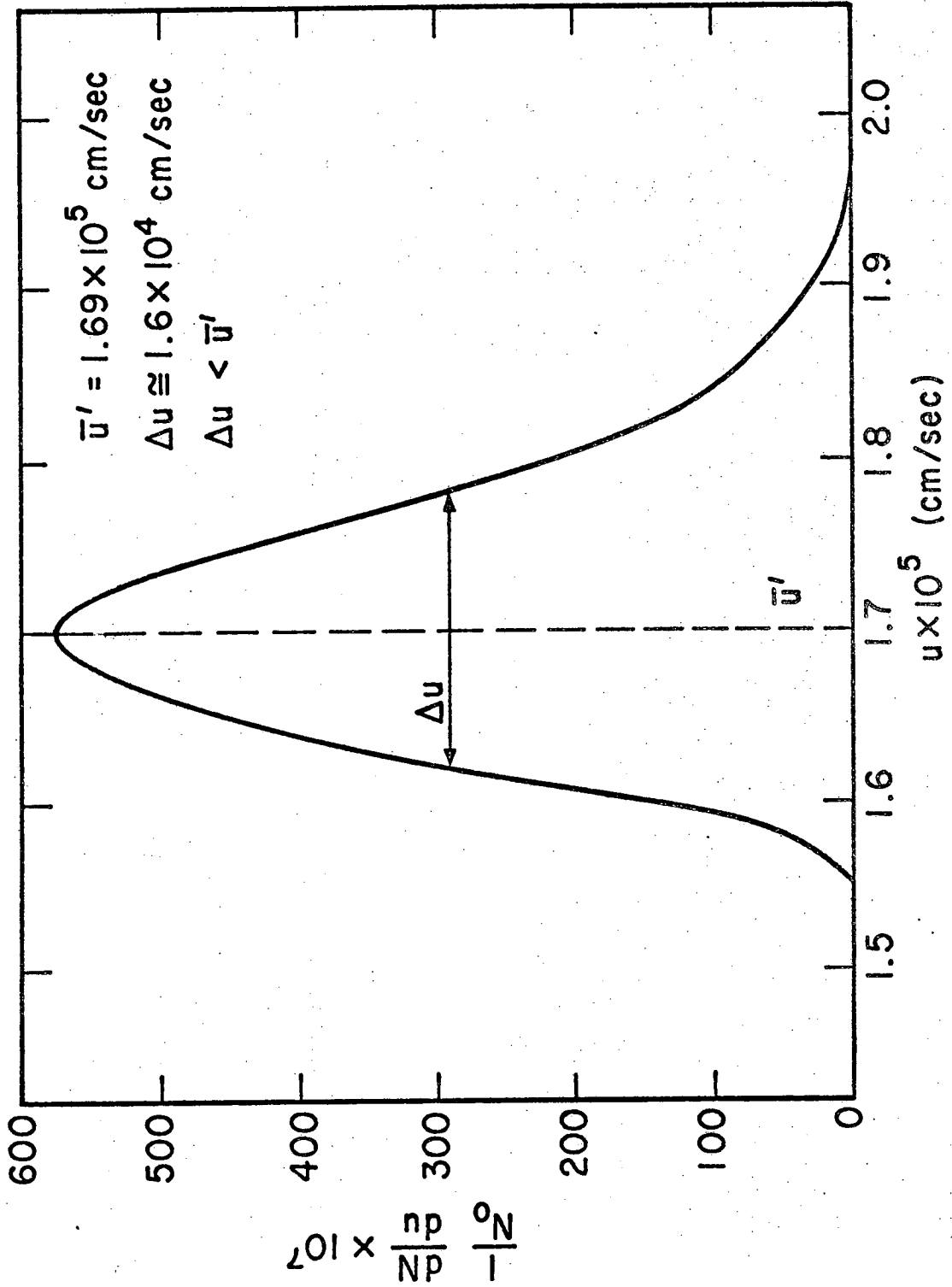
NBL 7211-7168

Fig. 4



XBL 7211-7169

Fig. 5



XBL 7211-7170

Fig. 6



LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720